A Study of Gas-Phase Reactions of Radical Cations of Mono- and Dihaloethenes with Alcohols by FT-ICR Spectrometry and Molecular Orbital Calculations: Substitution versus Oxidation

Andreas Nixdorf and Hans-Friedrich Grützmacher*[a]

Abstract: The ion-molecule reactions of the radical cations of vinyl chloride (**1**), vinyl bromide (**2**), 1,2-dichloroethene (**3**), 1,2-dibromoethene (**4**), 1,1-dichloroethene (**5**), and 1,1-dibromoethene (**6**) with methanol (MeOH) and ethanol (EtOH) have been studied by FT-ICR spectrometry. In the case of EtOH as reactant the oxidation of the alcohol to protonated acetaldehyde by a formal hydride transfer to the haloethene radical cation is the main process if not only reaction observed with the exception of the 1,2-dibromoethene radical cation which exhibits slow substitution. In secondary reactions the protonated acetaldehyde transfers the proton to EtOH which subsequently undergoes a well known condensation reaction of EtOH to form protonated diethyl ether. With MeOH as reactant, the 1,2-dihaloethene radical cations of $\mathbf{3}^{\cdot+}$ and $\mathbf{4}^{\cdot+}$ exhibit no reaction, while the other haloethene radical cations undergo the analogous reaction sequence of oxidation yielding protonated formaldehyde. Generally, bromo derivatives of haloethene radical cations react predominantly by substitution and chloro derivatives by oxidation. This selectivity can be understood by the thermochemistry of the competing processes which favors substitution of Br while the effect of the halogen substituent on the formal hydride transfer is small. However, the bimolecular rate constants and reaction efficiencies of the total reactions of the haloethene radical cations with both alcohols exhibit distinct differences, which do not follow the exothermicity of the reactions. It is suggested that the substitution reaction as well as the oxidation by formal hydride transfer proceeds by mechanisms which include fast and reversible addition of the alcohol to the ionized double bond of the haloethene radical cation which generates a β-distonic oxonium ion as the crucial intermediate. This intermediate is energetically excited by the exothermic addition and fragments either directly by elimination of a halogen substituent to complete the substitution process or rearranges by hydrogen migration before dissociation into the protonated aldehyde and a β-haloethyl radical. Reversible addition and hydrogen migrations within a long lived intermediate is proven experimentally by H/D exchange accompanying the reaction of the radical cations of vinyl chloride (**1**) and 1,1-dichloroethene (**5**) with CD_3OH. The suggested mechanisms are substantiated by ab initio molecular orbital calculations.

Keywords: FT-ICR spectrometry · ion-molecule reactions · nucleophilic substitution · radical ions · reaction mechanism

Introduction

Organic radical ions constitute an interesting and important class of reactive intermediates.[1] Many reactions, which are slow or even unknown for neutral reaction partners, turn out to be possible and useful for organic synthesis after transformation of one of the reactants into a radical ion. In particular, radical cations of arenes and alkenes are interesting intermediates. Their typical reactions are fast cycloaddition with neutral alkenes,[2] smooth reactions with electron rich nucleophiles,[3] and hydrogen transfer to and from appropriate hydrogen acceptors or donors.[4] Mass spectrometry is a convenient tool for mechanistic studies of the reactions of radical cations because they are easily generated in the gas phase from their neutral precursors by electron-impact ionization and can undergo subsequently reactions with neutral reactants either by chemical ionization (CI) mass spectrometry or, more adequately, by using one of the powerful techniques for the investigation of the kinetics of ion-molecule reactions.[5] One of these latter techniques is Fourier-transform ion-cyclotron resonance (FT-ICR) spectrometry. Here, the radical ions are trapped by a strong and homogeneous magnetic field, are "cooled" within the trapping cell to their ground state at room temperature, and react with selected gaseous compounds under carefully controlled conditions. Although one has to consider explicitly the special

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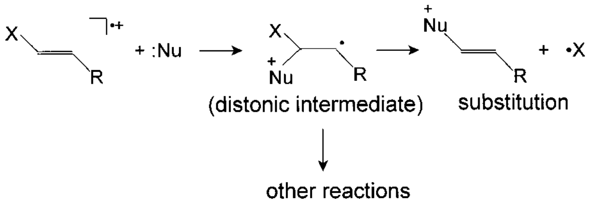
situation of reactions of isolated species in the diluted gas phase far from thermal equilibrium with the surroundings, this method gives valuable information about the reactivity of organic radical cations by direct observation of the radical cations and their (charged) products during the reactions and by the uncomplicated determination of rate constants of the reactions.

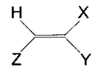
Earlier we investigated the reactions of the radical cations of halogenated arenes and alkenes with ammonia and simple amines as typical N-nucleophiles using FT-ICR.[6–8] In all these systems the main primary reaction observed is substitution of one halogen substituent to yield aromatic and vinylic ammonium ions, respectively. The kinetics of these ion-molecule reactions reveal that halogen substitution proceeds by an addition/elimination mechanism, and especially in the case of the radical cations of alkenes, addition of the N-nucleophile in the first reaction step occurs fast and without a noticeable activation barrier to generate energetically excited distonic ions as reaction intermediates (Scheme 1). Then, the fate of this excited intermediate determines the rate and the outcome of the total reaction.

Abstract in German: *Die Ion/Molekül-Reaktionen von Vinylchlorid (**1**), Vinylbromid (**2**), 1,2-Dichlorethen (**3**), 1,2-Dibromethen (**4**), 1,1-Dichlorethen (**5**) und 1,1-Dibromethen (**6**) mit Methanol (MeOH) und Ethanol (EtOH) wurden mit Hilfe der FT-ICR-Spektrometrie untersucht. Die Oxidation des Alkohols zum protonierten Aldehyd durch eine formale Hydrid-Übertragung zum Halogenethen-Radikalkation ist für EtOH die überwiegende oder sogar einzige Reaktion, mit Ausnahme des 1,2-Dibromethen-Radikalkations, das langsam unter Substitution reagiert. Der protonierte Acetaldehyd überträgt das Proton in einer Sekundärreaktion auf überschüssiges EtOH und leitet so eine bekannte Kondensationsreaktion des EtOH zum protonierten Diethylether ein. Mit MeOH erfolgt bei den ionisierten 1,2-Dihalogenethenen* $\mathbf{3}^{\bullet+}$ *und* $\mathbf{4}^{\bullet+}$ *keine Reaktion, während die Radikalkationen der übrigen Mono- und Dihalogenethene eine analoge Reaktionssequenz für die Oxidation von MeOH zum protonierten Formaldehyd zeigen. Generell reagieren die Radikalkationen der Br-substituierten Ethene vorwiegend unter Substitution, während bei den Cl-Derivaten die Oxidation überwiegt. Dieser Unterschied kann mit Hilfe der Thermochemie der konkurrierenden Reaktionswege erklärt werden. Die bimolekularen Geschwindigkeitskonstanten und die Effektivitäten der Gesamtreaktion der Radikalkationen mit beiden Alkoholen zeigen jedoch deutliche Unterschiede, die nicht alleine mit Hilfe der unterschiedlichen Exothermizität der Reaktionen erklärt werden können. Es wird gezeigt, dass sowohl Substitution als auch Oxidation nach einem Reaktionsmechanismus erfolgen, bei dem als entscheidende Zwischenstufe ein distonisches Oxoniumion durch schnelle und reversible Addition des Alkohols an die ionisierte Doppelbindung des Radikalkations entsteht. Dieses Zwischenprodukt ist aufgrund der exothermen Addition energetisch hoch angeregt und fragmentiert entweder durch Abspaltung eines Halogensubstituenten als Abschluss der Substitution oder nach Wasserstoffwanderungen durch Dissoziation in protonierten Aldehyd und β-Halogenradikal als Oxidationsprodukte. Reversible Addition des Alkohols und Wasserstoffwanderungen in einem langlebigen Additionsprodukt werden durch H/D-Austauschreaktionen bei der Reaktion der Radikalkationen von **1** und **5** experimentell nachgewiesen. Der vorgeschlagene Mechanismus wird durch theoretische Berechnungen gestützt.*



Scheme 1. Reaction pathway.

Besides N-nucleophiles, O-nucleophiles are frequent partners in the reactions of unsaturated radical cations since alcohols and ethers are often used as solvents. Therefore, we studied the ion-molecule reactions of unsaturated radical cations with some simple aliphatic alcohols as prototypical O-nucleophiles. So far we have not observed any reaction of the radical cations of halogenated benzenes with alcohols. However, fast ion-molecule reactions are observed by FT-ICR for the reactions of ionized halogenated alkenes and aliphatic alcohols. In this paper we report the results of a study of the reactions of the radical cations of the monohaloethenes vinyl chloride (**1**) and vinyl bromide (**2**) and of dihaloethenes, that is 1,2-dichloroethene (**3**), 1,2-dibromoethene (**4**), 1,1-dichloroethene (**5**), and 1,1-dibromoethene (**6**) with MeOH and EtOH by FT-ICR spectrometry. In addition, the experimentally observed reaction pathways were analyzed by a computation of critical points along the reaction coordinates using a high level of theory. The results demonstrate that in these reaction systems substitution of a halogen by the O-nucleophile competes with oxidation of the alcohol to the (protonated) aldehyde. However, experiment and theory show that both reactions originate from the same distonic ion generated as an excited intermediate by a fast exothermic addition of the O-nucleophile to the ionized alkene.



	X	Y	Z
1	Cl	H	H
2	Br	H	H
3	Cl	H	Cl
4	Br	H	Br
5	Cl	Cl	H
6	Br	Br	H

Results and Discussion

Reaction of monohaloethene radical cations $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$: The radical cations of the vinyl halides **1** and **2** yield efficient reactions with MeOH and EtOH as shown by the bimolecular rate constants k_{bi} and the reaction efficiencies *eff* presented in Table 1. In each case the decay of the radical cation follows strictly the kinetics of a pseudo-first order reaction, and kinetic plots of the four reactions are shown in Figure 1.

The bromo derivative $\mathbf{2}^{\bullet+}$ turns out to be substantially less reactive than the vinyl chloride radical cation $\mathbf{1}^{\bullet+}$ towards both alcohols. A similar effect has been observed for the reactions of these radical cations with ammonia.[7b] However, while in

Table 1. Bimolecular rate constants, k_{bi}, collision rate constants, k_{coll}, and reaction efficiencies, *eff*, of the reactions of vinyl halide radical cations $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ with MeOH and EtOH.

	MeOH			EtOH		
radical cation	k_{bi}[a]	k_{coll}[a]	*eff* [%]	k_{bi}[a]	k_{coll}[a]	*eff* [%]
$H_2C{=}CHCl^{\cdot+}(\mathbf{1}^{\cdot+})$	7.2	20.1	36	11.6	19.5	60
$H_2C{=}CHBr^{\cdot+}(\mathbf{2}^{\cdot+})$	3.4	18.6	18	7.0	17.5	36

[a] $\times 10^{-10}$ [$cm^3 molecule^{-1} s^{-1}$].

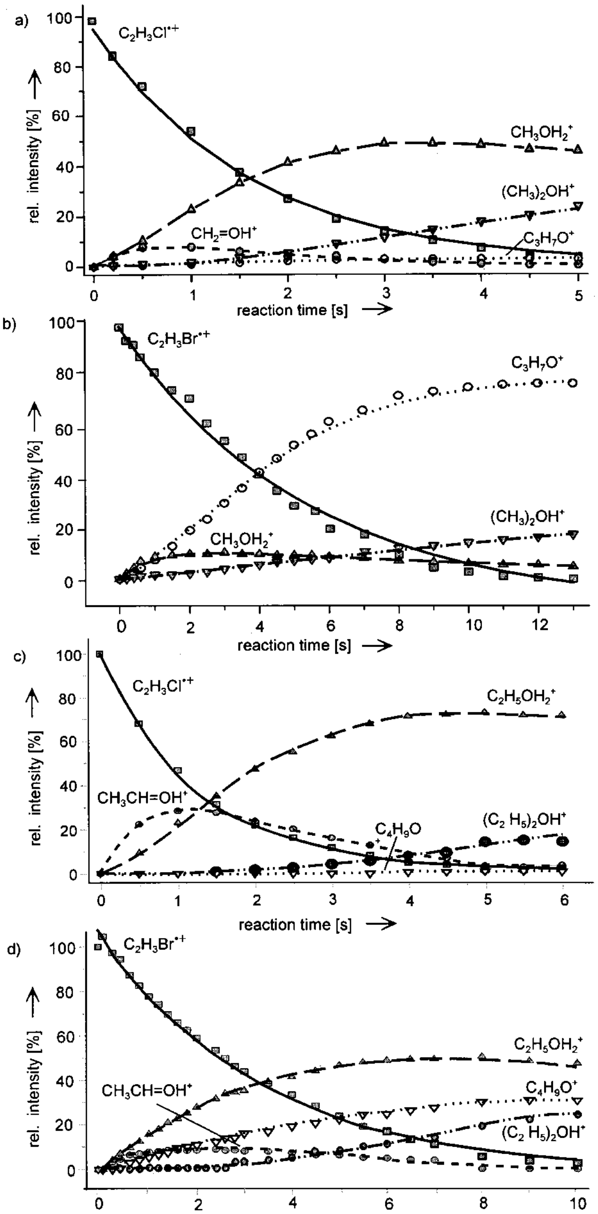
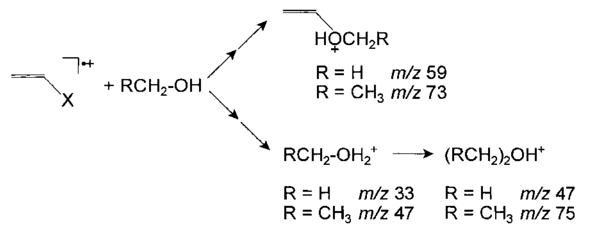


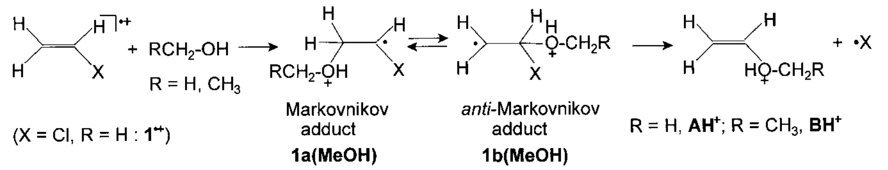
Figure 1. Kinetic plots of the reaction of the radical cations of vinyl chloride ($\mathbf{1}^{\cdot+}$), and vinyl bromide ($\mathbf{2}^{\cdot+}$) with MeOH and EtOH. a) $\mathbf{1}^{\cdot+}$/MeOH; b) $\mathbf{2}^{\cdot+}$/MeOH; c) $\mathbf{1}^{\cdot+}$/EtOH; d) $\mathbf{2}^{\cdot+}$/EtOH.



Scheme 2. The main products at the end of the reaction of the chloro ion $\mathbf{1}^{\cdot+}$.

the case of ammonia and other N-nucleophiles both monohaloethenes undergo mainly halogen substitution besides minor proton transfer, the product ion distribution of their reactions with MeOH and EtOH differs significantly. Substitution of the halogen in $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ by CH_3OH and C_2H_5OH gives rise to product ions $C_3H_7O^+$, *m/z* 59, and $C_4H_9O^+$, *m/z* 73, respectively, but these ions are observed with a high abundance only during the reactions of the bromo derivative $\mathbf{2}^{\cdot+}$. The main products at the end of the reaction of the chloro ion $\mathbf{1}^{\cdot+}$ (see Scheme 2) with MeOH are the ions *m/z* 33 (CH_5O by exact mass determination using high-resolution FT-ICR mass spectrometry) and *m/z* 47 (C_2H_7O by exact mass determination) or using EtOH as reactant the ions *m/z* 47 (C_2H_7O by exact mass determination) and *m/z* 75 ($C_4H_{11}O$ by exact mass determination). These ions are also formed during the reactions of $\mathbf{2}^{\cdot+}$ with these alcohols, but only as side products. In the case of MeOH the ion CH_5O, *m/z* 33, corresponds to protonated methanol $MeOH_2^+$, and it is known that this ion reacts further with MeOH to generate protonated dimethyl ether Me_2OH^+, *m/z* 47.[9] Analogously, in the EtOH reactions the ion C_2H_7O, *m/z* 47, corresponds to protonated ethanol $EtOH_2^+$ which condensates with another EtOH molecule to yield protonated diethyl ether Et_2OH^+, *m/z* 75. These consecutive reactions of the protonated alcohols ROH_2^+ are clearly visible in the kinetic plot of Figure 1 by the sigmoidal shape of the intensity curves of the respective protonated ether R_2OH^+. However, proton transfer from the haloethene radical cation to the alcohols can not be a primary reaction because MeOH (proton affinity (PA) = 754.3 $kJ mol^{-1}$)[10] and EtOH (PA = 776.4 $kJ mol^{-1}$)[10] are not strong bases, and an estimation of the reaction enthalpy shows that the deprotonation of $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ by MeOH is endothermic for all possible halovinyl radicals. Indeed, a closer inspection of the initial stages of the reaction reveals ions CH_3O^+, *m/z* 31, and $C_2H_5O^+$, *m/z* 45, respectively, as the primary reaction products and the precursors of the protonated alcohols. This especially apparent in the reactions of $\mathbf{1}^{\cdot+}$ with EtOH (see Figure 1c). As shown by their acidity the ions CH_3O^+, *m/z* 31, and $C_2H_5O^+$, *m/z* 45, correspond to protonated formaldehyde and acetaldehyde, respectively. Thus, the primary reactions of the vinyl halide radical cations $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ with MeOH and EtOH are nucleophilic substitution of the halogen by an alcohol molecule and oxidation of the alcohol to the respective protonated aldehyde.

The direct substitution of the halogen of the ionized vinyl halides $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ by MeOH and EtOH gives rise to O-protonated vinyl methyl ether $\mathbf{AH}^+$ and vinyl ethyl ether $\mathbf{BH}^+$, respectively. By analogy with the mechanism of the halogen substitution by N-nucleophiles,[7, 8] an addition/elimination mechanism (Scheme 3) is suggested also for the substitution reaction of $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ with MeOH and EtOH. The PA of vinyl ethers for O-protonation are experimentally



Scheme 3. Addition/elimination mechanism suggested for the substitution reaction of $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ with MeOH and EtOH.

not available and can not be used for a determination of the enthalpy of formation, ΔH°_f, of $\mathbf{AH}^+$ and $\mathbf{BH}^+$. Therefore, the enthalpy of reaction, ΔH°_r, both for the total reaction and the individual reaction steps, was obtained by molecular orbital calculation of relevant stationary points along the reaction coordinate at the FC-UMP4(STDQ)/D95**//UHF/D95** level of theory for odd electron species and FC-MP4(STDQ)/D95**//RHF/D95** level for even electron species. The results are given in Table 2, and the resulting minimum energy reaction path (MERP) is shown in Figure 2.

Table 2. Ab initio calculation for the construction of the MERPs of the reaction of vinyl chloride radical cation, $\mathbf{1}^{\cdot+}$, and MeOH.

	FC-(U)MP4/(STDQ)/D95** [hartree]	ZPE [kJ mol⁻¹]	E_{therm} [kJ mol⁻¹]
$H_2C{=}CHCl^{\cdot+}$ ($\mathbf{1}^{\cdot+}$)	– 537.0348188	117	127
MeOH	– 115.4352078	145	157
1a(MeOH)	– 652.5133765	277	295
1b(MeOH)	– 652.5051894	273	291
1c(MeOH)	– 652.5023446	278	294
$H_2C{=}CH{-}O^+(H)CH_3$	– 192.912873	272	286
$Cl^\cdot$	– 459.5681221	0	4
TS(MeOH shift)	– 652.4973731	267	287
$H_3C{-}CHCl^\cdot$	– 537.9560795	147	157
$ClH_2C{-}CH_2^\cdot$	– 537.9507668	145	157
$H_2C{=}OH^+$	– 114.5157816	115	123
TS(H shift)	– 652.4614882	266	281

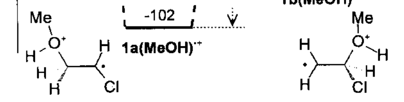
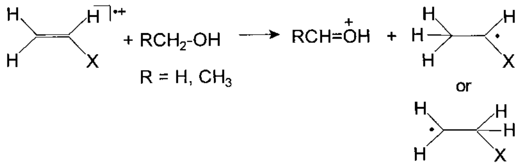


Figure 2. Minimum energy reaction path for the substitution process of the radical cation of vinyl chloride, $\mathbf{1}^{\cdot+}$, and MeOH (numbers indicate relative enthalpy in kJ mol⁻¹).

According to these calculation the substitution of the Cl atom of $\mathbf{1}^{\cdot+}$ by MeOH is exothermic by 19 kJ mol⁻¹. The experimental ΔH°_f of $\mathbf{2}^{\cdot+}$ exceeds that of $\mathbf{1}^{\cdot+}$ by 28 kJ mol⁻¹, and by the difference of the ΔH°_f a Br atom is 9 kJ mol⁻¹ more stable than a Cl atom.[10] Using these differences of ΔH°_f of the reactants and products of the substitution reaction of $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ with MeOH, the latter reaction is estimated to be distinctly exothermic by 56 kJ mol⁻¹. This increase in exothermicity explains the experimentally observed prevalence of $\mathbf{2}^{\cdot+}$ for substitution, since no extra activation barrier is found by the ab initio calculation along the MERP of the substitution reaction. By exchanging MeOH by EtOH in the reactions of $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ it is expected that the ethyl group stabilizes the ionic reaction product $\mathbf{BH}^+$ more than the neutral reactant alcohol.[11] Therefore, the substitution reaction of $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ with ETOH are both expected to be slightly more exothermic than with MeOH.

The addition of the alcohol to the ionized double bond gives rise to two isomeric distonic adduct ions depending on the regiochemistry of the addition. In analogy to the Markovnikov rule the product formed by addition of the alkoxy moiety to the unsubstituted C atom of $\mathbf{1}^{\cdot+}$ or $\mathbf{2}^{\cdot+}$ is denoted as the Markovnikov adduct in which the radical site is stabilized by the adjacent halogen. Hence, this adduct is more stable than the anti-Markovnikov adduct in which the radical site corresponds to a primary radical. In the case of the addition of MeOH to $\mathbf{1}^{\cdot+}$ the addition step is calculated to be very exothermic (Markovnikov adduct **1a(MeOH)**$^{\cdot+}$ by 103 kJ mol⁻¹; anti-Markovnikov adduct **1b(MeOH)**$^{\cdot+}$ by 83 kJ mol⁻¹). In the diluted gas phase of the FT-ICR cell this energy stays in **1a(MeOH)**$^{\cdot+}$ and **1b(MeOH)**$^{\cdot+}$ as excess energy which is used to drive the further reaction of the excited distonic ions. However, only the less stable **1b(MeOH)**$^{\cdot+}$ is able to eliminated the Cl atoms without further rearrangement. We found a transition state for the interconversion of **1a(MeOH)**$^{\cdot+}$ and **1b(MeOH)**$^{\cdot+}$ corresponding to a barrier of 35 kJ mol⁻¹. This barrier for an 1,2-shift of MeOH is considerably smaller than the barrier of 115 kcal mol⁻¹ obtained for the 1,2-shift of the NH_3 group in the adducts of NH_3 to $\mathbf{1}^{\cdot+}$.[7b] A 1,2-shift of H_2O in the adduct of H_2O and ethene radical cation is known to occur through re-dissociation into an ion/neutral complex and not through a transition state.[12] An analogous complex may be involved also in the interconversion of **1a(MeOH)**$^{\cdot+}$ and **1a(MeOH)**$^{\cdot+}$. In any case, isomerization between the two adducts is fast because they are highly excited by the exothermic addition step. Therefore, it is remarkable that oxidation of the alcohols by a formal hydride transfer to the vinylic radical cations and production of protonated aldehydes competes successfully with substitution.

Protonated aldehydes and ketones, that is, hydroxycarbenium ions, are abundant fragment ions in the electron ionization mass spectra of alcohols. However, the generation of these ions during the reactions of $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ with alcohols via oxidation by direct electron transfer and subsequent fragmentation of the molecular ions of the alcohols is excluded because of the large difference between the ionization energies (*IE*) of the vinyl halides **1** and **2** and MeOH or EtOH.[10] The oxidation of MeOH and EtOH to protonated aldehydes by the vinyl halide radical cations $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ occurs by hydride abstraction specifically from the α-C atom. Enthalpies of formation, ΔH_f°, are known for the reactants vinyl halide radical cation $\mathbf{1}^{\bullet+}$ or $\mathbf{2}^{\bullet+}$ and MeOH or EtOH as well as for the final products chloroethyl radical or bromoethyl radical and protonated formaldehyde or protonated acetaldehyde.[10, 13] These data have been used to calculate the enthalpy of reaction, ΔH_r, of the oxidation.[14] The results show that hydride transfer from MeOH to $\mathbf{1}^{\bullet+}$ is exothermic by 13 kJ mol^{-1} only if the more stable 1-chloroethyl radical is formed (see Scheme 4). Similarly, the hydride transfer from MeOH to $\mathbf{2}^{\bullet+}$ is exothermic by 8 kJ mol^{-1} only for formation of the 1-bromoethyl radical. Thus, oxidation of MeOH by hydride transfer to $\mathbf{1}^{\bullet+}$ is about as exothermic as substitution of the Cl atom, while in the case of $\mathbf{2}^{\bullet+}$ substitution of the Br atom is distinctly more exothermic than the oxidation. This is in line with the experimental observation that oxidation is much more effective in the reactions of $\mathbf{1}^{\bullet+}$ while substitution is the main reaction of $\mathbf{2}^{\bullet+}$. Because of some ambiguity of the experimental ΔH_f° of $\mathbf{1}^{\bullet+}$ and $\mathbf{AH}^+$ the enthalpy of reaction of hydride transfer and the ΔH_f° of relevant stationary points along the MERP (see below) have been calculated by molecular orbital theory at the same level as for substitution. The results are included in Table 2 and the resulting MERP is shown Figure 3. By these calculations the hydride transfer from MeOH to $\mathbf{1}^{\bullet+}$ under formation of $CH_2{=}OH^+$ and the 1-chloroethyl radical is exothermic by 4.8 kJ mol^{-1}, in good agreement with the value derived from the selected experimental values.[14] For EtOH as reactant the hydride transfer is calculated from the available experimental data to be strongly exothermic both for $\mathbf{1}^{\bullet+}$ ($\Delta H_r^\circ = -92$ kJ mol^{-1}) and $\mathbf{2}^{\bullet+}$ ($\Delta H_r^\circ = -87$ kJ mol^{-1}) for the formation of an 1-haloethyl radical and even exothermic for the formation of a β-haloethyl radical as the neutral product.



Scheme 4. Hydride transfer reaction.

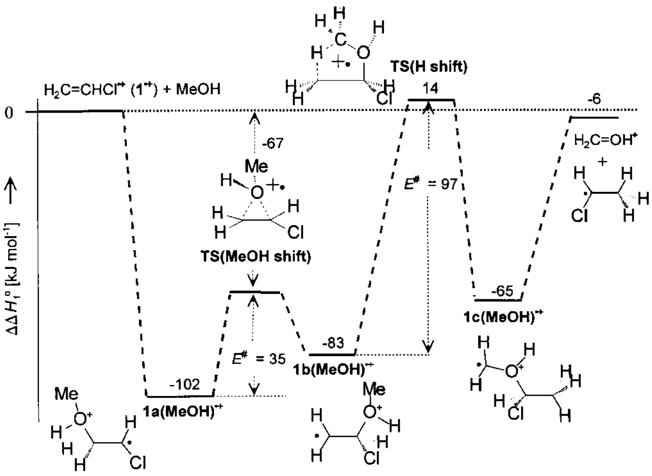
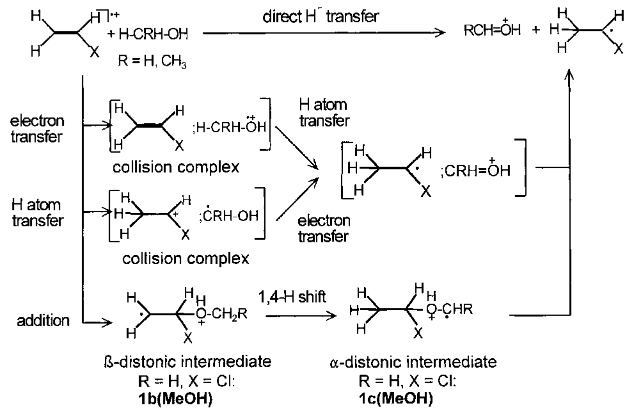


Figure 3. Minimum energy reaction path for the oxidation process of the radical cation of vinyl chloride, $\mathbf{1}^{\bullet+}$, and MeOH (numbers indicate relative enthalpy in kJ mol^{-1}).

In principle the mechanism of the oxidation process can either correspond to a direct ("true") hydride transfer from the alcohol to the alkene radical cation or to a separate transfer of an electron and a hydrogen atom (or even something "in between"), spanning a mechanistic scenario from a synchronous process to a stepwise process (Scheme 5).



Scheme 5. Mechanistic reaction pathway.

However, in contrast to hydride abstraction by carbenium ions a significant energy barrier is expected for a hydride abstraction by a radical cation.[15] The total oxidation process is only slightly exothermic but nevertheless competes with exothermic substitution. Therefore, a direct hydride transfer which is handicapped by an additional activation barrier is not likely to occur. The alternative, a two-step mechanism, requires under the conditions of a diluted gas phase of an FT-ICR cell that the two reaction steps occur in a single collision complex. There is no chance for the second step to proceed if the products of the first step escape from the complex, and the ionic primary products would be detected in the mass spectrum. Several examples of ion-molecule reactions involving multi-step mechanisms are known which proceed in a single long-lived collision complex.[16] As mentioned before, charge exchange between $\mathbf{1}^{\bullet+}$ or $\mathbf{2}^{\bullet+}$ and MeOH or EtOH is strongly endothermic (47–98 kJ mol^{-1}), and it is very unlikely that the energy released during the complex formation between $\mathbf{1}^{\bullet+}$ or $\mathbf{2}^{\bullet+}$ and MeOH or EtOH is large enough to compensated this endothermicity to allow electron transfer as the initial step within the complex. The attempt to calculate the unknown complexation energy between $\mathbf{1}^{\bullet+}$and MeOH by ab initio methods failed because immediate collapse of the complex to the distonic addition product. The other possible two-step mechanism mediated by a long-lived collision complex is hydrogen atom abstraction from the α-CH_2 group of MeOH or EtOH by the radical cation $\mathbf{1}^{\bullet+}$ or $\mathbf{2}^{\bullet+}$ and electron transfer in the complex of the products of this step, the α-hydroxyalkyl radical and the halogen substituted ethyl cation, to generate the final products. The ΔH_f° of haloethyl cations $C_2H_4Cl^+$ and $C_2H_4Br^+$ have been determined by appearance energy determination using photoionization and energy resolved electron impact,[17] but have not included into the NIST data base ref. [10] because of some ambiguity in the ΔH_f^o of the neutral precursors and in the structure of the ions.[17b] In the case of cation $C_2H_4Cl^+$ it has been proven, that the most stable isomer corresponds to the α-chloroethyl cation CH_3CHCl^+.[18] Accepting the published values of ΔH_f^o (CH_3CHCl^+) of 828[17a]–833 kJ mol^{-1}[17b] the hydrogen abstraction from MeOH by $\mathbf{1}^{\cdot+}$ is endothermic by at least 39 kJ mol^{-1}, which again has to be compensated for by the energy released during complex formation between $\mathbf{1}^{\cdot+}$ and MeOH. Thus, also the second pathway of a complex-mediated mechanism of the formal hydride transfer is unlikely, although it cannot be rigorously excluded. However, there is in another a multi-step mechanism in which the reactants are first covalently bonded in the initial step followed by electron and hydrogen transfer in this intermediate, which is depicted in Scheme 5. In fact, this intermediate corresponds to the β-distonic oxonium ion **1b(MeOH)**$^{\cdot+}$ which is also generated in the first step of the substitution process by nucleophilic addition of the aliphatic alcohol with anti-Markovnikov orientation to the double bond of the ionized vinyl halide $\mathbf{1}^{\cdot+}$ or $\mathbf{2}^{\cdot+}$. Subsequent internal H abstraction by the radical site converts the energetically excited β-distonic ion eventually into an α-distonic oxonium ion **1c·(MeOH)**$^{\cdot+}$ which fragments into the final products haloethyl radical and protonated aldehyde. This mechanism is attractive because it involves the same intermediate, which is generated in the collision complex of the reactants without an activation barrier, both for substitution and oxidation accounting for the effective competition between both reactions. Further, hydrogen rearrangements as depicted in Scheme 5 are common in energetically excited distonic ions, in particular if more stable α-distonic ions are generated.[19]

We searched by ab initio methods for a transition state for the 1,4-H shift **1b(MeOH)**$^{\cdot+} \rightarrow$ **1c(MeOH)**$^{\cdot+}$. Using FC-UMP4(STDQ)/D95**//UHF/D95** an activation barrier of 97 kJ mol^{-1} was found (Table 2). As can be seen from the representation of the calculated MERP in Figure 3, this transition state exceeds the energy level of the reactants by 14 kJ mol^{-1} which would make the total oxidation process of MeOH by $\mathbf{1}^{\cdot+}$ very slow. However, the reliability of the $\Delta\Delta H_f^o$ of transition states obtained by the molecular orbital calculation at the present level of theory is probably only ± 20 kJ mol^{-1} for open shell systems. Indeed, a preliminary calculation of the energy of the transition state of the 1,4-H shift using a larger basis set than D95** lowers the activation barrier by about 13 kJ mol^{-1}.[20] Thus, the activation energy for the 1,4-H shift may be in fact somewhat lower than originally calculated which allows competition between substitution of Cl and oxidation by a formal hydride transfer as observed experimentally.

To get some experimental information about hydrogen rearrangements during the oxidation of aliphatic alcohols by the vinyl halide radical cations, the reactions of the radical cation of trideuterated vinyl chloride $[\mathbf{D_3}]\mathbf{1}^{\cdot+}$ with MeOH and of $\mathbf{1}^{\cdot+}$ with 1,1,1-trideuteromethanol [D$_3$]MeOH were studied. In the first case only primary product ions $CH_2{=}OH^+$ and subsequently secondary ions $CH_3OH_2^+$ were observed, while in the second case only ions $CD_2{=}OH^+$ and $CD_3OH_2^+$ are detected, confirming experimentally the absence of any direct proton transfer from $\mathbf{1}^{\cdot+}$ to MeOH. However, in reaction of $\mathbf{1}^{\cdot+}$ with [D$_3$]MeOH ions $C_2H_2DCl^{\cdot+}$ are observed at 1–4 s reaction time, although only in low abundances of 2–4%. These deuterated ions disappear at longer reaction times by reaction with [D$_3$]MeOH, but it is clear that they have been generated by H/D exchange of the vinyl chloride radical cations with the trideuteromethyl group of the neutral reactant during the reaction. Besides H/D exchange this result proves unambiguously a reversible first step which is in complete agreement with the suggested mechanisms for the halogen substitution reaction and alcohol oxidation.

Reaction of dihaloethene radical cations $\mathbf{3}^{\cdot+}$, $\mathbf{4}^{\cdot+}$,$\mathbf{5}^{\cdot+}$ and $\mathbf{6}^{\cdot+}$: The rate constants, k_{bi}, and reaction efficiencies, *eff*, of the reactions of the radical cations of 1,2-dichloroethene ($\mathbf{3}^{\cdot+}$) (mixture of *cis*/*trans* isomers),[21] of 1,2-dibromoethene ($\mathbf{4}^{\cdot+}$) (mixture of *cis*/*trans* isomers), of 1,1-dichloroethene ($\mathbf{5}^{\cdot+}$) and of 1,1-dibromoethene ($\mathbf{6}^{\cdot+}$) with MeOH and EtOH are collected in Table 3, and the kinetic plots of the reactions of $\mathbf{5}^{\cdot+}$ with MeOH and EtOH and $\mathbf{6}^{\cdot+}$ with MeOH are shown in Figure 4.

Table 3. Bimolecular rate constants, k_{bi}, collision rate constants, k_{coll}, and reaction efficiencies, *eff*, of the reactions of dihaloethene radical cations $\mathbf{3}^{\cdot+}$–$\mathbf{6}^{\cdot+}$ with MeOH and EtOH.

	MeOH			EtOH		
radical cation	k_{bi}[a]	k_{coll}[a]	*eff* [%]	k_{bi}[a]	k_{coll}[a]	*eff* [%]
$ClHC{=}CHCl^{\cdot+}$($\mathbf{3}^{\cdot+}$)		nr[b]		3.8	17.6	22
$BrHC{=}CHBr^{\cdot+}$($\mathbf{4}^{\cdot+}$)		nr[b]		0.7	16.2	4
$H_2C{=}CCl_2^{\cdot+}$($\mathbf{5}^{\cdot+}$)	1.6	18.3	8	7.2	17.6	41
$H_2C{=}CBr_2^{\cdot+}$($\mathbf{6}^{\cdot+}$)	0.9	17.6	6	6.5	16.2	40

[a] $\times 10^{-10}$ [cm^3 molecule^{-1} s^{-1}]. [b] nr = no reaction.

The radical cations $\mathbf{3}^{\cdot+}$ and $\mathbf{4}^{\cdot+}$ do not react at all with MeOH, very likely because the expected reactions are endothermic. This is confirmed by estimation of ΔH_r^o for the oxidation by hydride transfer for the dichloro derivative $\mathbf{3}^{\cdot+}$, for which the ΔH_f^o of the relevant species are available in the literature.[22] From these data the oxidation of MeOH by hydride transfer to $\mathbf{3}^{\cdot+}$ is endothermic by about 42 kJ mol^{-1} (and remains endothermic even if the uncertainties of the data are taken into account). One can assume by comparison with the reactions of $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ that substitution of a Br atom by MeOH is energetically more favorable by about 30 kJ mol^{-1}, but this decrease of the enthalpy of reaction is obviously not enough to allow an efficient reaction between the 1,2-dibromo derivative $\mathbf{4}^{\cdot+}$ and MeOH. In contrast to the reactions with MeOH, both $\mathbf{3}^{\cdot+}$ and $\mathbf{4}^{\cdot+}$ carry out reactions with EtOH, although with very different efficiency and with different main products. As discussed before, hydride abstraction from EtOH is much more energetically favorable than from MeOH, accordingly $\mathbf{3}^{\cdot+}$ reacts with EtOH exclusively by oxidation via hydride transfer. The reaction is fast with an efficiency of 22% and is estimated to be exothermic by about 37 kJ mol^{-1}.[23] In contrast, the total reaction of the $\mathbf{4}^{\cdot+}$ with EtOH is slow with an efficiency of only 4%, and the main

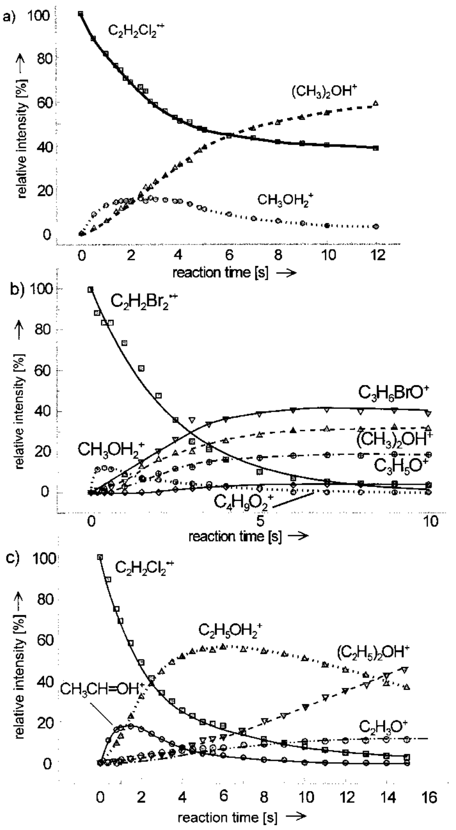
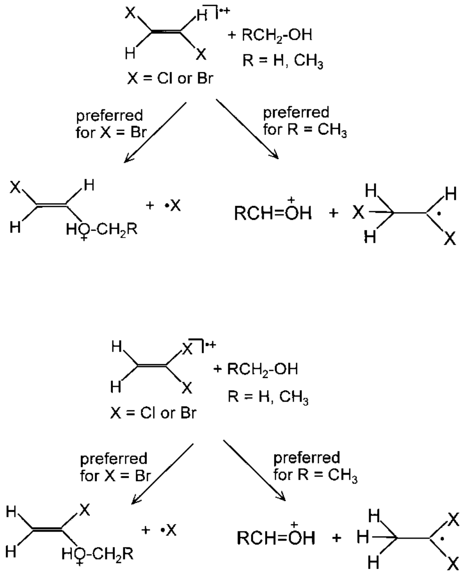


Figure 4. Kinetic plots of the reaction of the radical cations of 1,1-dichloroethene ($\mathbf{5}^{\bullet+}$), and 1,1-dibromoethene ($\mathbf{6}^{\bullet+}$), with MeOH and EtOH. a) $\mathbf{5}^{\bullet+}$/MeOH; b) $\mathbf{6}^{\bullet+}$/MeOH; c) $\mathbf{5}^{\bullet+}$/EtOH.

reaction pathway is substitution of one bromo substituent. This is in line with the expectation, that a hydride abstraction by $\mathbf{4}^{\bullet+}$ is more endothermic because a reduced stabilization of the resulting alkyl radical by the Br substituent, and that substitution of Br is energetically more favorable than that of Cl. However, the small reaction efficiency indicates that even in the case of $\mathbf{4}^{\bullet+}$ substitution is thermoneutral or even slightly endothermic.

The 1,1-dihaloethene radical cations $\mathbf{5}^{\bullet+}$ and $\mathbf{6}^{\bullet+}$ undergo slow reactions with MeOH and fast reactions with EtOH. With the latter reactant only oxidation of EtOH by hydride abstraction is observed, and no product ions of substitution are detected. With MeOH, the 1,1-dichloro derivative $\mathbf{5}^{\bullet+}$ reacts only by a hydride transfer, while the 1,1-dibromo derivative $\mathbf{6}^{\bullet+}$ yields mainly protonated bromovinyl methyl ether $CH_2{=}CBr\text{-}OH^+\text{-}CH_3$, by substitution. The hydride transfer from EtOH to $\mathbf{5}^{\bullet+}$ exhibits a reaction efficiency of 22% and that from MeOH only 8%, in agreement with an estimation of the reaction enthalpy of these two processes of $-63\,kJ\,mol^{-1}$ and $+15\,kJ\,mol^{-1}$, respectively. Unexpectedly, the reaction of $\mathbf{5}^{\bullet+}$ and MeOH is not complete, as can be seen from the kinetic plot in Figure 4, but finishes at 60–70% conversion. This effect is discussed in a separate paper,[24] where it is proven that the unreactive fraction of ions $C_2H_2Cl_2^{\bullet+}$ generated from $\mathbf{5}^{\bullet+}$ consists of the isomeric 1,2-dichloroethene radical cation $\mathbf{3}^{\bullet+}$. This unprecedented rearrangement of an organic radical cation by 1,2-H and 1,2-Cl shifts occurs parallel to the slow reaction of $\mathbf{5}^{\bullet+}$ with MeOH and is catalyzed by MeOH. However, it should be noted that this effect is observed specifically for the reaction of $\mathbf{5}^{\bullet+}$ with MeOH, and neither in the reaction of $\mathbf{5}^{\bullet+}$ with EtOH nor in the reactions of the 1,1-dibromo derivative $\mathbf{6}^{\bullet+}$ with both alcohols.

The differences of the preferred reaction channel (halogen substitution versus oxidation by hydride transfer) observed for dichloroethene and dibromoethene radical cations $\mathbf{3}^{\bullet+}$, $\mathbf{4}^{\bullet+}$, $\mathbf{5}^{\bullet+}$, and $\mathbf{6}^{\bullet+}$ as well as the effects of using MeOH or EtOH as the neutral reactant can again be understood by the different effects of the Cl and Br substituent on the enthalpy of the two reaction channels competing for the fragmentation of the distonic ion generated in the first reaction step by nucleophilic addition of the alcohol to the ionized dihaloethene (Scheme 6).



Scheme 6. Reaction step leading to ionized dihaloethene.

On the one side, EtOH instead of MeOH reduces definitely the reaction enthalpy for hydride transfer from the α-C atom while only a small effect on the reaction enthalpy of the substitution is expected. Thus, all dihaloethene radical cations with exception of the 1,2-dibromo derivative $\mathbf{4}^{\bullet+}$ undergo a fast reaction with EtOH by hydride abstraction and formation of protonated acetaldehyde. A Br substituent stabilizes the haloalkyl radical, which is the neutral product of the hydride transfer, less than a Cl substituent. Thus, at least two geminal Br substituents as in $\mathbf{6}^{\bullet+}$ are necessary to make hydride transfer from EtOH exothermic owing to the concomitant formation of an 1,1-dibromoethyl radical. Therefore, $\mathbf{4}^{\bullet+}$, which produces a haloethyl radical with only one Br substituent at the radical site, shows only minor hydride abstraction from EtOH. On the other side, substitution of Br by the alcohol is energetically favored over substitution of Cl. As a consequence $\mathbf{4}^{\bullet+}$ reacts slowly with EtOH by substitution. Similarly, neither a single chlorine nor a single bromine substituent at the radical site stabilizes the haloalkyl radical enough to make the hydride abstraction from MeOH exothermic. Hence, no reaction is observed between $\mathbf{3}^{\bullet+}$ or

4$^{\cdot+}$ and MeOH, and in the case of the 1,1-dihaloethene radical cations and MeOH only the 1,1-dichloro derivative **5**$^{\cdot+}$ reacts slowly by hydride transfer and formation of protonated formaldehyde, while the main reaction path of the 1,1-dibromo derivative **6**$^{\cdot+}$ is substitution. These effects demonstrate again a direct competition between substitution and oxidation also of the dihaloethene radical cations, as predicted by the suggested mechanism with the addition product as the common intermediate for both reactions.

The slow reaction of the 1,1-dihaloethene radical cations **5**$^{\cdot+}$ and **6**$^{\cdot+}$ with MeOH give the chance to examine the reaction mechanism further by using [D$_3$]MeOH and MeOD as reactants. The mechanistic picture developed so far for the reactions of haloalkene radical cations with nucleophiles postulates as a first reaction step a fast exothermic and reversible addition of the nucleophile to the ionized double bond. The reactions of **5**$^{\cdot+}$ and **6**$^{\cdot+}$ with MeOH are slow because the final reaction steps are only slightly exothermic or even endothermic. However, the initial addition of MeOH which generates the distonic oxonium ion should be similar exothermic as for the monohaloethene radical cations **1**$^{\cdot+}$ and **2**$^{\cdot+}$. Thus, the small efficiencies of the total reaction of **5**$^{\cdot+}$ and **6**$^{\cdot+}$ with MeOH imply a high reversibility of the first addition step and the possibility that the excited distonic intermediate undergoes reversible hydrogen atom migrations before dissociation back to the reactants. Obviously this is the case for **5**$^{\cdot+}$ as shown by the kinetic plot of its reaction with [D$_3$]MeOH in Figure 5. During this reaction the consecutive formation of $C_2HDCl_2^{\cdot+}$ and $C_2D_2Cl_2^{\cdot+}$[25] in substantial abundances up to 20% is observed. This proves unambiguously that a reversible addition of [D$_3$]MeOH to **5**$^{\cdot+}$ occurs initially and that the β-distonic intermediate formed lives long enough for H/D-exchange reactions to occur before dissociation back to reactants. Further, no H/D-exchange is observed during the of **5**$^{\cdot+}$ with MeOD, as expected from the proposed reaction mechanism.

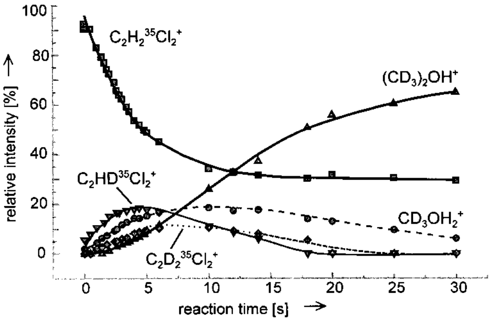


Figure 5. Kinetic plot of the reaction of the radical cation of 1,1-dichloroethene (**5**$^{\cdot+}$) with [D$_3$]MeOH.

Interestingly, no H/D exchange is observed during the reaction of the 1,1-dibromo derivative **6**$^{\cdot+}$ with [D$_3$]MeOH. This reaction results mainly in substitution of one bromine atom of **6**$^{\cdot+}$ and oxidation by hydride abstraction is a minor process. However, an H/D-isotope effect on the branching ratio is observed for [D$_3$]MeOH as reactant. The branching ratio of substitution versus oxidation of 1.9:1 in the case of MeOH increases to 5.3:1 in the case of [D$_3$]MeOH, corresponding to a H/D-isotope effect of 2.8 which is very likely only due to the hydride abstraction. This isotope effect shows that the hydrogen rearrangement of the β-distonic intermediate into the α-distonic oxonium ion, which precedes directly the dissociation into the products of the hydride transfer reaction, is the rate limiting step of the oxidation of MeOH by **6**$^{\cdot+}$. In this case no H/D-exchange is expected to accompany the hydride transfer reaction of **6**$^{\cdot+}$.

Conclusion

The study of the ion-molecule reaction of mono- and dihaloethene radical cations with MeOH and EtOH as simple O-nucleophiles adds further information to the understanding of the reactivity of unsaturated organic radical cations towards nucleophiles. The typical reaction of these radical cations is the substitution of a halogen substituent by the nucleophile, and this has been proven to proceed by an addition/elimination mechanism. In the case of alcohols as weak O-nucleophiles the substitution reaction has to compete with oxidation of the primary alcohols to the corresponding protonated aldehydes. Formally, this oxidation corresponds to the transfer of a hydride ion to the haloethene radical cation. However, it is suggested that the oxidation takes place as an "inner sphere" process to account for the experimental results, in particular for the exchange between the hydrogens of the haloethene radical cation and of the methyl group of MeOH which is proved by using [D$_3$]MeOH as reactant. According to this mechanism the oxidation involves three reaction steps. In the first step the same β-distonic oxonium ion as for the substitution process is formed by addition of the alcohol to the ionized double bond. However, instead of a fragmentation by loss of a halogen substituent the β-distonic intermediate rearranges in the second step by hydrogen atom migration into an α-distonic ion which eventually dissociates in the third step into the protonated aldehyde and a halolethyl radical as the oxidation products. In the case of the reaction of ionized vinyl chloride **1**$^{\cdot+}$ with MeOH the stationary points along the MERP of this mechanisms as well as the MERP of the substitution process have been calculated by ab initio methods, and the results agree reasonably with the suggested mechanisms. In particular, no activation barrier has been found for the addition of the O-nucleophile to the ionized C=C double bond, in complete analogy to the addition of N-nucleophiles. Using EtOH as reactant instead of MeOH makes the oxidation process considerably more energetically favorable, and in addition the activation barrier for the rearrangement of the α-hydrogen in the distonic intermediate is considerably reduced. Consequently, the oxidation of EtOH by the formal hydride transfer dominates the reaction with most of the haloethene radical cations studied. Substituting the chlorine atom of the haloethene radical cation by a bromine atom influences predominantly the substitution by decreasing the enthalpy of reaction for this process. By these two effects the variation of the total rate constants of the haloethene radical cations and of the branching ratio between substitution and oxidation can be understood.

Finally it should be emphasized that the ion-molecule reactions of the haloethene radical cations with simple aliphatic alcohols are a further instructive example of the importance of the fragmentation of an energetically excited intermediate which is generated by the addition of an electron rich partner to the ionized double bond of the alkene derivative. Ab initio calculation demonstrate that this addition step is very exothermic in the reactions studied here, although not so much as in the case of the N-nucleophiles studied before. However, the total reactions of the haloethene radical cations **1**$^{\cdot+}$–**6**$^{\cdot+}$ in particular with MeOH are only moderately exothermic or even slightly endothermic. Thus, the rate constants and the outcome of these reactions are much more affected by variations of the enthalpy of reaction than in the case of the reaction with N-nucleophiles.

The fact, that the gas phase ion-molecule reactions of the haloethene radical cations are controlled by an energetically excited intermediate is of importance if the present results are used to predict or understand the same reactions in solution. No activation barrier has been observed for the addition step, hence one can expect fast formation of the β-distonic addition product also in solution. However, deactivation of excited species is fast in solution. Therefore, the β-distonic intermediate should be trapped as a reactive but long-lived species in solution. In the case of the reaction of the alkene radical cations with alcohols the reactive centers of the β-distonic intermediate correspond to an alkyl radical and a protonated ether. Therefore, deprotonation is a very likely follow-up reaction in solution which leaves a β-alkoxy radical as the reactive species. The final fate of this radical will depend on its individual structure, but in most cases hydrogen abstraction by the radical will be the final step yielding the adduct of the alcohol as the final product.

Experimental Section

Compounds: Vinyl chloride (**1**) (99.5 %), vinyl bromide (**2**) (98 %), 1,2-dichloroethene (**3**) (mixture of *cis*/*trans* isomers, >97 %), 1,2-dibromoethene (**4**) (mixture of *cis*/*trans* isomers, >97 %), 1,1-dichloroethene (**5**) (>97 %) as well as methanol and ethanol (>99.5 %, Merck) used as the neutral reagent are commercially available as pure compounds and were used without further purification. 1,1-Dibromoethene (**6**), which slowly polymerizes upon storage, was freshly prepared from 1,1,2-tribromoethane as described in ref. [7d].

FT-ICR spectrometry: Ion-molecule reactions were investigated with a Spectrospin Bruker CMS 47X FT-ICR instrument[26] equipped with 4.7 Tesla magnet, an external EI/CI-ion source[27] and a cylindrical ICR Infinity cell.[28] The radical cations $C_2H_3X^{\cdot+}$ and $C_2H_2X_2^{\cdot+}$ (X = Cl, Br) were generated in the external ion source by electron impact at a nominal electron energy of 18–27 eV. All ions formed were transferred into the FT-ICR cell containing the respective alcohol at an appropriate constant background pressure of 10^{-8}–10^{-7} mbar. The ions were isolated by applying a broad band ejection ("chirp ejection", 88 V_{p-p}, 80 µs) followed by a series of single frequency pulses ("single shots", 14 V_{p-p}, 1.6 ms) to select only one isotopomer of $^{12}C_2{}^1H_3X^{\cdot+}$ and $C_2H_2X_2^{\cdot+}$ (X = ^{35}Cl or ^{79}Br, if not stated otherwise). The isolated radical cations were thermalized by collision with argon introduced into the ICR cell by a pulsed valve as described before.[7c] After a delay time of 500 ms for removing argon any fragment ions or product ions formed during the cooling period were ejected again by single shots, and special care was taken to avoid any translational excitation of the isolated vinyl halide radical cations during this procedure. The time for the reaction of ions $CH_2{=}CHX^{\cdot+}$ with the alcohol was varied from 1.5 ms to 15 s. Then, all ions in the FT-ICR cell were excited by an frequency sweep of 88 V_{p-p} with a step width of 7.8 kHz and an excitation pulse time of 8 µs. The mass spectra were recorded by 32 K data points for 20–30 different reaction times. Each mass spectrum is the average of at least 16 data acquisition sequences. After exponential multiplication of the time domain signal and Fourier transformation the peak intensities of the magnitude spectra were normalized to the sum of all ion detected at that reaction time and plotted *versus* the reaction time ("kinetic plot").

The pseudo-first order rate constants k_{exp} were obtained from the slope of a logarithmic plot of the relative reactant ion intensity versus the reaction time and the bimolecular rate constants k_{bi} were calculated by taking into account the number density of ammonia in the FT-ICR cell. The number density was calculated from the pressure of the neutral reagent gas in the FT-ICR cell which was measured by an ion gauge located between the FT-ICR cell and the turbomolecular pump. The readings of the ion gauge were corrected for the sensitivity of respective alcohol as the neutral gas,[29] and the pressure within the FT-ICR cell was calibrated by measuring the rate constant for $NH_3^{\cdot+} + NH_3 \rightarrow NH_4 + {}^{\cdot}NH_2$ ($k_{bi} = 21 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}[30]). The normalized efficiency (in %) of the ion-molecule reaction is given by $k_{bi}/k_{coll} \times 100$, where the collision rate constant k_{coll} was calculated using the method of Su and Chesnavich.[31] The reproducibility of the experimental rate constants is very good, but the error of the absolute rate constants obtained by the procedure was estimated to about 30 % mainly because of the uncertainty of the measurement of the partial pressure of the neutral reactant within the FT-ICR cell.

Computational details: Ab initio molecular orbital calculations were performed by the GAUSSIAN 92 program[32] on a RS/6000 workstation or a SNI S600/20 computer. The geometries of all species were fully optimized at the Hartree–Fock level with the D95** basis set[33] using gradient procedures.[34] For double-zeta level calculations a Huzinaga basis set[35] for the bromine atom (13s10p4d/6s5p2d) was used with an additional d-function exponent of 0.389. The spin-unrestricted Hartree–Fock formalism was used for the open shell radical cations and the restricted Hartree–Fock formalism for the closed shell species. Harmonic vibrations were computed to characterize properly the stationary points on the potential energy hypersurfaces as minima (for equilibrium structures) or first order saddle points (for transition state structures) and to estimate the zero-point vibrational energy E^0_{vib}. The latter energy was scaled by an empirical factor of 0.9 to correct the systematic overestimation of vibrational frequencies by the Hartree–Fock calculations.[36] The frozen core approximation FC-(U)MPn was used for all perturbation calculations. Single point calculations were performed at the (U)MP4(SDTQ)/D95** level of theory. Unfortunately, a spin unrestricted wave function may contain contributions from unwanted spin states which distort the potential hypersurface. For that reason spin projected FC-UMP4 energies (PMP4) have been calculated to obtain improved values of the potential energy. The absolute energy was corrected for the zero-point vibrational energy to calculate the reaction enthalpy ΔH^0_r at 0 K. The enthalpies of formation, ΔH^{298}_f at 298 K were derived from the corresponding calculated values of ΔH^0_f using standard statistical thermodynamics.[37]

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[11] This follows from the increase of PA(EtOH) compared with PA(MeOH) or of PA(Et_2O) compared with PA(EtOMe) by 22 kJ mol^{-1} and 20 kJ mol^{-1}, respectively.[10] Analogously, the product ions $\mathbf{AH}^+$ and $\mathbf{BH}^+$ correspond to a protonated methyl ether and diethyl ether.

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[14] The hydride transfer reaction with MeOH as reactant is slightly *endothermic* (by 0.9 kJ mol^{-1} and 6.4 kJ mol^{-1} for $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$, respectively) if the most recent NIST value of ΔH_f° ($CH_2{=}OH^+$) = 718.0 kJ mol^{-1}[10] is used, but *exothermic* by using the value of 703.5 kJ mol^{-1} from the previous NIST Standard Reference Database 19A (**1994**) for the calculation. Since a significant hydride transfer reaction, which proves an *exothermic* ion-molecule reaction, is observed experimentally even for $\mathbf{2}^{\bullet+}$, the present NIST value of ΔH_f° ($CH_2{=}OH^+$) is very likely too large by a few kJ mol^{-1}. With EtOH as hydride donor the reaction is always calculated strongly exothermic anyway. The following values (in kJ mol^{-1}) have been used: ΔH_f° ($\mathbf{1}^{\bullet+}$) = 999, $\mathbf{2}^{\bullet+}$ = 1027, ΔH_f° (MeOH) = −201.1, ΔH_f° (EtOH) = −235.3, ΔH_f° ($\mathbf{AH}^+$) = ΔH_f° ($CH_2{=}OH^+$) = 703.5, ΔH_f° ($\mathbf{BH}^+$) = ΔH_f° ($CH_3CH{=}OH^+$) = 582.8, ΔH_f° ($CH_3CHCl^\bullet$) = 80.8, ΔH_f° ($ClCH_2CH_2^\bullet$) = 95.4, ΔH_f° ($CH_3CHBr^\bullet$) = 114.3, ΔH_f° ($BrCH_2$-$CH_2^\bullet$) = 135.1.

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[21] The *E* and *Z* isomers of $\mathbf{3}^{\bullet+}$ exhibit no difference in their reactions with NH_3 and CH_3NH_2 (ref. [7a]), in line with the suggested reaction mechanism. Hence, mixtures of the stereoisomers have been used in this work.

[22] The following data have been used: ΔH_f° (**3**) = 1.7 kJ mol^{-1} and *IE* (**3**) = 9.64 (ref. [10]) giving ΔH_f° ($\mathbf{3}^{\bullet+}$) = 932 kJ mol^{-1}, ΔH_f° (MeOH) = −201.1 kJ mol^{-1} (ref. [10]), ΔH_f° ($\mathbf{AH}^+$) = 703.5 kJ mol^{-1} (NIST Standard Reference Database 19A (**1994**)), and ΔH_f° (CH_2Cl-$CHCl^\bullet$) = 69 kJ mol^{-1} (derived from ref. [12b]).

[23] The following data have been used: ΔH_f° (**3**) = 1.7 kJ mol^{-1} and *IE* (**3**) = 9.64 (ref. [10]) giving ΔH_f° ($\mathbf{3}^{\bullet+}$) = 932 kJ mol^{-1}, (EtOH) = −235.3 kJ mol^{-1} (ref. [10]), ΔH_f° ($\mathbf{BH}^+$) = 590.8 kJ mol^{-1} (ref. [10]), and ΔH_f° ($CH_2Cl{-}CHCl^\bullet$) = 69 kJ mol^{-1} (derived from ref. [12b]).

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